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CRYSTALLIZATION OF SnO_2 -MODIFIED $\text{K}_2\text{O} - \text{Li}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ GLASSES

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Glass-formation in potassium-lithium-aluminosilicate system is studied. The effect of tin oxide on the crystallization properties of $\text{K}_2\text{O} - \text{Li}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ glasses is studied. The crystallization properties of transparent and opacified glasses are compared. The phase composition of the products of their crystallization is studied.

There is only a limited number of works devoted to the role of SnO_2 in silicate systems and its effect on their physical – chemical and crystallization properties. Virtually no attention has been devoted to this question in the scientific literature on the effect of oxides on the properties of glass. There are only individual publications where positive properties of tin dioxide, such as the capability of increasing the chemical resistance (especially resistance to alkali) and mechanical performance, and its role as an opacifier in glass and an initiator of crystallization for obtaining glass ceramics [1 – 3]. This effect is similar to that of ZrO_2 in silicate glasses. However, it should be noted that the solubility of SnO_2 in a silicate melt is higher than that of ZrO_2 , so that its effect is more multifaceted.

Works performed under the direction of Professor L. A. Zhunina devote the greatest attention to the role of SnO_2 in silicate glasses (primarily, with pyroxene composition) [4 – 7]. Data on the effect of 3 – 5% (molar content) of SnO_2 on liquation and crystallization are presented in these works. It is also established that SnO_2 cannot substitute for SnO_2 isomorphically in the structure of silicate glass, and consequently on crystallization it easily forms an autonomous phase — cassiterite.

It should be noted that in general the effect of SnO_2 on the properties of glass is very complex and depends on the coordination state of tin, which, in turn, is determined by its concentration, the conditions under which synthesis occurs, and the glass composition.

According to the rule governing the ratio of the ionic radii of cations and anions, four- and six-fold coordination is possible for the Sn^{4+} ion. However, the $[\text{SnO}_4]$ tetrahedron is much larger in size than the $[\text{SiO}_4]$ tetrahedron, so that the incorporation of $[\text{SnO}_4]$ groups into the silicon-oxygen framework is problematic, in any case very limited. The six-fold coordination of Sn^{4+} is more stable, so that SnO_2

is easily released in the form of cassiterite crystals from the melt.

The possibilities for introducing 10.5 – 12.5%² SnO_2 , which increases the adhesion of a glass ceramic coating with the surface of a metallic base, are analyzed in [8]. This is very important for obtaining tin-containing coatings on metal substrates. The effect of SnO_2 on the physical-chemical and crystallization properties of $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ and $\text{K}_2\text{O} - \text{Li}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ glass has not been studied at all. Interest in this problem arose in connection with the fact that these glasses are used as a base for obtaining leucite-containing (leucite $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) glass-crystalline materials, serving as a base for coatings when producing metallo-ceramic articles for stomatological application (US Patent No. 6761760). Such coatings are formed on the basis of several layers, of which the first one, called the opaque layer, must meet special opacification requirements, degree of matching with respect to the CLTE, the mechanical strength, and chemical resistance.

In a previous work [9] we established that the active release of leucite during heat-treatment of $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ glasses, whose composition lies in the crystallization field of leucite, occurs only with the additional introduction of Li_2O , which, evidently, promotes the activation of diffusion processes as a result of a decrease of viscosity of the glass melts and, possibly, the development of metastable liquation phenomena. However, the crystallized materials obtained on the basis of these glasses were characterized by high values of the CLTE (from 16×10^{-6} to $20 \times 10^{-6} \text{ K}^{-1}$), which is higher than the values required for the opacifier deposited on nickel-chromium ($14.1 \times 10^{-6} \text{ K}^{-1}$) and cobalt-chromium ($14.4 \times 10^{-6} \text{ K}^{-1}$) alloys.

According to some data, leucite can exist in two polymorphous modifications — cubic high-temperature and tetragonal low-temperature, which are characterized by sub-

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² Here and below: mass content.

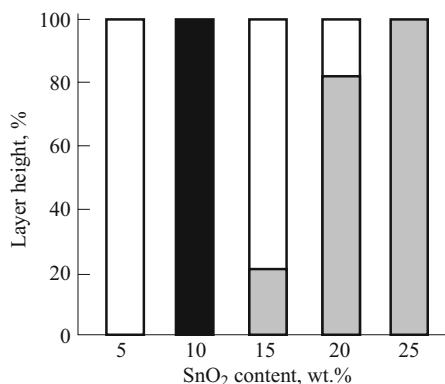


Fig. 1. Distribution of transparent, opalescent, and opaque layers in the glasses: (□) transparent glass; (■) slight opalescence; (▒) opacified glass.

stantially different values of the CLTE. Apparently, the high values of the CLTE of crystallized materials are due to the release of leucite in the low-temperature form, whose CLTE is of the order of $20 \times 10^{-6} \text{ K}^{-1}$ and according to [10] about $28.5 \times 10^{-6} \text{ K}^{-1}$. The CLTE of the high-temperature form of leucite is considerably lower — about $10 \times 10^{-6} \text{ K}^{-1}$. The transition from one modification to the other occurs (according to different data) in the temperature range $600 - 625^\circ\text{C}$. Unfortunately, because of the negligible differences of the interplanar distances in the diffraction patterns of both forms it is very difficult to determine from x-ray phase analysis the leucite form which is released.

In addition, because of the high content of alkali-metal oxides, the chemical resistance of the crystallized glasses obtained was found to be too low. Consequently, to increase it and at the same time decrease the CLTE of leucite-containing glass crystalline materials in the optimal composition, containing 10% Li_2O , which promotes active release of leucite during heat-treatment, from 5 to 30 parts by mass SnO_2 (above 100%) was introduced. The glasses were synthesized at temperatures $1450 \pm 10^\circ\text{C}$ with a holding time at this temperature of 2 h.

The glasses containing 5 and 10% SnO_2 were founded well and fined, remaining transparent (5%) or slightly opalescent (10%) on cooling (Fig. 1). Increasing the SnO_2 content to 15–20% resulted in the appearance of two layers in the crucible — a transparent or slightly opalescent layer on top and an opacified layer on the bottom. The glasses containing 25–30% SnO_2 were found to be completely opacified.

Microanalysis of the transparent glass layers showed that they contain up to 7% SnO_2 . Evidently, these are the limiting values of the solubility of SnO_2 in the experimental glasses. Slight opalescence appears even for 10% SnO_2 . For higher SnO_2 content the excess content of this compound precipitates in the form of fine crystals from the supersaturated melt on cooling or remains unreacted. This is clearly seen in the photographs of the structure of the glasses obtained in a scanning electron microscope (Fig. 2). Small, light-colored cassiterite crystals precipitated from the melt and larger ini-

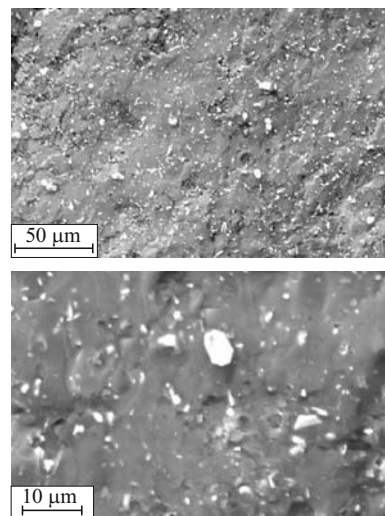


Fig. 2. Electron-microscope photographs of the structure of glass containing 15% SnO_2 and 10% Li_2O .

tial crystals can be seen. Since the density of cassiterite (6.950 kg/m^3) is higher than that of glass, the cassiterite particles settle and two layers appear in the crucible — a transparent layer at the top and an opacified layer in the form of a suspension at the bottom. The presence of only one crystalline phase in the opalescent and opacified glasses — cassiterite — is confirmed by x-ray diffraction.

The glasses obtained after averaging were subjected to heat-treatment according to the following regime: 950°C with 1 h holding and 1050°C with 5 h holding to obtain a glass-crystalline material (Belarus Patent No. 10337). All products of crystallization were characterized by a fine-crystalline glass-ceramic type structure and were white. According to XPA, the main crystalline phases were leucite, cassiterite, and lithium metasilicate. All phases are clearly distinguishable in electron-microscope photographs of the crystallized samples: light-colored bulk or prismatic crystals) cassiterite (Fig. 3a), dark) leucite crystals (Fig. 3b), and needle-shaped) lithium metasilicate crystals (Fig. 3c). Local microanalysis also confirms this: the light- and dark-colored crystals contain up to 92% SnO_2 and up to 82% leucite, respectively.

It was of interest to compare the crystallization properties of transparent and opacified glasses. Figure 4 displays DTA curves for both types of glasses with different initial content of SnO_2 .

The presence of two clearly expressed exothermal effects — at $750 - 780$ and $870 - 880^\circ\text{C}$ — is observed on the DTA curves of the transparent glasses. According to the XPA data, the first exo-effect is due to the precipitation of lithium metasilicate and the second one is due to leucite and cassiterite crystallizing out practically simultaneously. The latter two phases start to precipitate at $800 - 810^\circ\text{C}$. The cassiterite precipitates as a result of supersaturation of the liquid phase.

Two exo-effects in the same temperature intervals are recorded in the DTA curves of the glasses. The first exo-effect

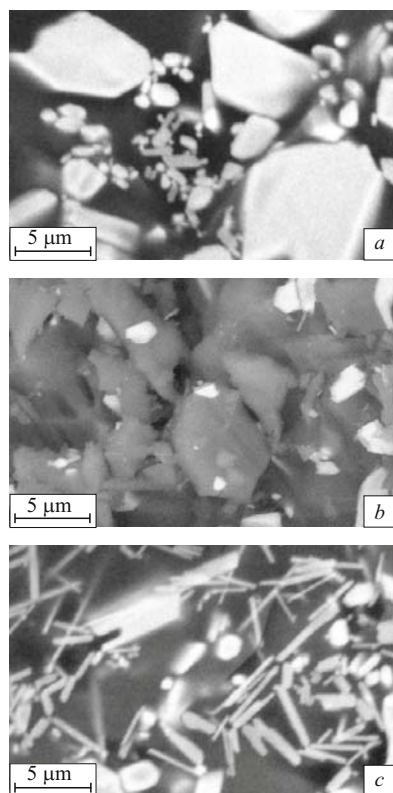


Fig. 3. Electron-microscope photographs of the structure of glass-crystalline material containing 15% SnO_2 .

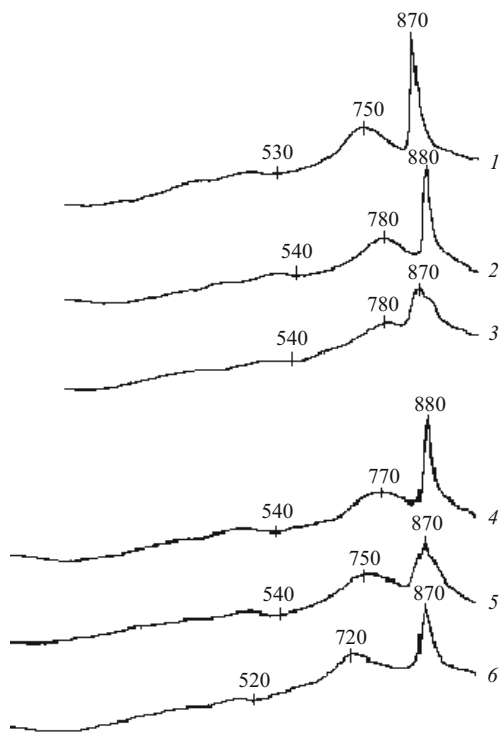


Fig. 4. DTA curves of the transparent (1 – 3) and opacified (4 – 6) glasses, containing SnO_2 in the following amounts: 10% (1), 15% (2, 4), 20% (3, 5), and 25% (6).

in the temperature interval 740 – 800°C is due to the precipitation of lithium metasilicate and the second one (870 – 880°C) is due to the precipitation of crystalline leucite. Cassiterite crystals are present in all compositions initially, i.e., before heat-treatment.

Differences are observed in the crystallization of the transparent and opacified glass layers with respect to the leucite precipitation intensity. In transparent glasses, the SnO_2 content in the initial glass has an appreciable effect on the height of the exo-effect associated with leucite, but in the opacified glass such an effect does not occur and the height of the leucite exo-peak remains practically constant, and corresponds to the height of the peak in transparent glasses with the maximum SnO_2 content (20 – 25%).

In summary, the amount of the leucite formed in transparent glasses can be regulated by introducing different amounts of SnO_2 ; there is no such possibility for opacified glass.

Since leucite sharply increases the CLTE of the glass ceramics, its content must be limited. Consequently, the optimal compositions can be the ones into which 20 – 25% SnO_2 is introduced.

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